Organoboranes. IV. The Displacement Reaction with Organoboranes Derived from the Hydroboration of Branched-Chain Olefins. A Contrathermodynamic Isomerization of Olefins

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Abstract: Organoboranes react readily with less volatile olefins in refluxing diglyme solution to liberate a more volatile olefin while forming the organoborane of the less volatile olefin. The rate of the displacement reaction appears to be independent of the concentration of the displacing olefin, in agreement with the proposed mechanism involving a prior dissociation of the organoborane into olefin and dialkylborane. The latter then reacts with the displacing olefin present in relatively large excess. The scope of this displacement reaction was explored by applying it to a number of organoboranes synthesized *in situ* by the hydroboration of selected representative olefins. No isomerization of the olefins, or of the organoboranes, is observed in the process. Consequently, it becomes possible to hydroborate internal olefins, isomerize the boron to the terminal position with a slight catalytic excess of hydride, and then displace the olefin from the boron with a suitable displacing olefin. In this manner, 3-ethyl-2-pentene, with a double bond in the stable tertiary position, was readily converted into 3-ethyl-1-pentene, with a terminal double bond. Therefore, hydroboration–isomerization–displacement provides a simple procedure to achieve the movement of a double bond from the interior of a carbon chain to the terminal position—a contrathermodynamic isomerization of olefins.

One of the more interesting aspects of the chemistry of organoboranes is the formation of olefins from such organoboranes by displacement with other olefins (eq 1).[2,3] This property, coupled with their facility in isomerization,[3,4] suggests useful applications in the synthesis of olefins.

$$(RCH_2CH_2)_3B + 3R'CH{=}CH_2 \longrightarrow 3RCH{=}CH_2\uparrow + (R'CH_2CH_2)_3B \qquad (1)$$

Isomerization of olefins by acidic catalysts or strong bases leads to the formation of the more stable olefins containing the double bond preferentially in an internal position of the chain. The synthesis of pure terminal olefins by elimination reactions, involving the use of strong acids or bases, frequently presents experimental difficulties. In a sense, the displacement reaction (eq 1) can be considered to be a new type of elimination reaction, not involving strong acids or bases, and it offers promise as a convenient means of synthesizing olefins.

However, very little work has been done on exploring the scope of this new reaction. In particular, it appeared important to examine the possibility of displacing relatively labile olefin structures without rearrangement. Accordingly, we undertook to convert a number of branched-chain olefins into the corresponding organoboranes *via* the hydroboration, and then to subject the products to the displacement technique, in order to establish whether the olefin thus recovered exhibited any isomerization under the reaction conditions.

When we discovered that no olefin isomerization occurred, we turned our attention to the possibility of combining the displacement reaction with the hydroboration–isomerization reaction previously explored in detail[3,4] to achieve a simple, general procedure for the conversion of internal acyclic olefins into the corresponding terminal olefins.[5]

Results

In previous studies the displacement reaction was brought about by heating the isolated organoborane and the displacement olefin at relatively high temperatures.[2,3] The organoboranes are reactive materials, highly sensitive to atmospheric oxygen. There would be obvious advantages for a synthetic procedure if it were possible to carry out the displacement reaction in the same medium utilized for the hydroboration and isomerization reactions. Indeed, preliminary experiments revealed that diglyme is an excellent medium for the reaction and the displacement reaction proceeds at a satisfactory rate in the refluxing solvent (162°).

Before deciding on a standard procedure for the study of the displacement reaction, it appeared desirable to establish the effect of the concentration of the displacing olefin on the rate of displacement. Accordingly, 100 mmoles of 1-pentene was converted into the corresponding organoborane by internal hydroboration in diglyme, the reaction mixture was attached to a Todd micro column, and 1-decene was added for the displacement. The reaction mixture was brought to reflux and the pentene distilled was collected and measured. It was noted that the use of 120 mmoles of 1-decene produced 76 mmoles of pentene in 5 hr, whereas 220 mmoles of 1-decene produced only slightly more, 83 mmoles. Since the reflux temperature was slightly higher in the latter case, it was concluded that

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(1) Postdoctorate research associate on funds provided by the Ethyl Corp.

(2) R. Köster, *Angew. Chem.*, **68**, 3831 (1956); R. Köster, *Ann.*, **618**, 31 (1958).

(3) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6434 (1959).

(4) H. C. Brown and G. Zweifel, *ibid.*, **88**, 1433 (1966).

(5) A preliminary communication reporting some of these results has appeared: H. C. Brown and M. V. Bhatt, *ibid.*, **82**, 2074 (1960).

the rate of the displacement reaction is essentially independent of the concentration of the displacing olefin.

Structural Variations in the Displaced Olefin. The standardized procedure selected was similar to the above. The olefin in question, 100 mmoles, was hydroborated in diglyme solution using 20% excess hydride. Then 150 mmoles of 1-decene was added. The reaction mixture was heated and the displaced olefin was recovered as formed with the aid of the Todd micro column. The rate of recovery of the olefin with time was noted. Gas chromatographic examination of the product, as individual fractions were collected, established its composition at various stages of the reaction.

The rate of distillation of the olefins from the reaction mixture depends upon a number of mechanical variables which could not be rigidly controlled in our experiments (see the Experimental Section). Consequently, the time required for each displacement should be considered to provide only an approximate measure of the relative ease with which various structural types undergo displacement.

The displacement of pentene from the organoborane derived from 1-pentene was essentially completed in 5 hr, with a recovered yield of 83%. Analysis of the product showed 91% 1-pentene and 9% 2-pentene. The organoborane from 2-pentene was more reactive. In this case, displacement required 2.5 hr and there was realized an 87% yield of pentene, 98% 2- and 2% 1-.

2-Methyl-2-butene also was displaced rapidly from its organoborane (in 3 hr) with the product consisting of 99% 2-methyl-1-butene and 1% 2-methyl-2-butene. On the other hand, the displacement of 3-methyl-1-butene again was slow.

Both 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene were displaced relatively easily, both being obtained in essentially 100% isomeric purity. Similarly, 3-ethyl-2-pentene was rapidly obtained from its hydroboration product.

The data establish that there is no significant isomerization of the organoborane during the displacement reaction and that di- and trisubstituted olefins are displaced with somewhat greater ease than terminal olefins. Indeed, it was observed that in the displacement of the organoborane from 1-pentene, the 2-pentene in the product tended to be present in larger amounts in the initial fractions of the collected product.

These results are summarized in Table I.

Structural Variations in the Displacing Olefin. It was of interest to examine the relative effectiveness of different structures in the displacing olefin to achieve the displacement reaction. 1-Octene, 2-octene, and 2,4,4-trimethyl-1-pentene were selected for examination, and the organoboranes from 2-methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1-butene were subjected to displacement by each of these displacing olefins.

The di- and trisubstituted olefins, 2-methyl-1-butene and 2-methyl-2-butene, both were displaced easily by all three displacing olefins. The differences observed in the ease of displacement were minor and within the range of the experimental uncertainties of the experimental procedure.

On the other hand, the displacement of the terminal olefin, 3-methyl-1-butene, was slower and large differences were observed in the rates. The apparent effectiveness decreased in the order 1-octene > 2-octene > 2,4,4-trimethyl-1-pentene.

Table I. Displacement of Olefin from Its Hydroboration Product with 1-Decene[a]

Organoborane from olefin	Time, hr	Yield, %	Olefin product, % 1-	2-
1-Pentene	5	76	88	12[c]
2-Pentene	2.5	87	2	98[d]
2-Methyl-1-butene	3	79	99	1
3-Methyl-1-butene	9	65	98	2
2,4,4-Trimethyl-1-pentene	5	89	100	0
2,4,4-Trimethyl-2-pentene[b]	5	80	0	100
3-Ethyl-2-pentene[b]	3	68	11	89

[a] In the standard procedure, 100 mmoles of olefin was hydroborated with 120 mmoles of hydride and displaced in refluxing diglyme with 150 mmoles of 1-decene. [b] In these cases 100 mmoles of olefin was hydroborated with 150 mmoles of hydride and displaced with 200 mmoles of 1-decene. [c] 7% *trans*, 5% *cis*. [d] 50% *trans*, 48% *cis*.

These results are summarized in Table II.

Table II. Displacement of the Methylbutenes from Their Hydroboration Products with Selected Olefins[a]

Organoborane from olefin	Displacing olefin	Time, hr	Yield, %	Olefin product, % 1-	2-
2-Methyl-1-butene	1-Octene	3.5	70	100	0
	2-Octene	3.5	74	94	6
	TMP[c]	3.5	81	99	1
2-Methyl-2-butene[b]	1-Octene	3.5	75	1	99
	2-Octene	3.5	74	0	100
	TMP[c]	4.5	...[d]	2	98
3-Methyl-1-butene	1-Octene	9	56	87	13
	2-Octene	14	54	84	16
	TMP[c]	3.5	13	75	19[e]

[a,b] See corresponding footnotes in Table I. [c] 2,4,4-Trimethyl-1-pentene. [d] A portion of product was lost, so the yield could not be determined. However, it was comparable to the previous cases. [e] Also 6% 2-methyl-1-butene.

Selective Displacement. These data indicated that it might be possible to achieve selective displacements. To test this, a mixture of 100 mmoles each of 2-methyl-1-butene and 3-methyl-1-butene was hydroborated and displaced with 200 mmoles of 2,4,4-trimethyl-1-pentene. An 87% yield of methylbutenes was obtained which on analysis showed 79% 2-methyl-1-butene, 9% 2-methyl-2-butene, and 12% 3-methyl-1-butene. Therefore 2-methyl-1-butene is preferentially displaced, but the reaction is not as selective as one would like.

Hydroboration–Isomerization–Displacement. Finally, we turned our attention to the possibility of combining hydroboration–isomerization[3,4] with displacement to achieve a simple conversion of internal into terminal olefins. The procedure worked very well. The olefin was hydroborated internally in the diglyme solution, the mixture was refluxed for 1 hr to achieve isomerization, and then 1-decene was added to achieve displacement.

In this way, 2-pentene was converted in 77% yield to 91% 1-pentene and 9% 2-pentene. Similarly, 4,4-dimethyl-2-pentene was converted into 4,4-dimethyl-1-pentene in a yield of 73%. Of especial interest is the observation that the highly stable tertiary double bond of 3-ethyl-2-pentene can be moved readily to the terminal position. Thus, the hydroboration–isomerization–displacement of 3-ethyl-2-pentene provided 3-ethyl-1-pentene in a yield of 82% and a purity of 98%.

An unexpected development was the relatively low yield of 63% realized in applying the procedure to 2,4,4-trimethyl-2-pentene, whereas the displacement of 2,4,4-trimethyl-1-pentene had been shown previously to proceed in excellent yield. However, this proved to be the result of a rapid cyclization reaction during the isomerization stage.[6] When the isomerization was carried out under conditions which would avoid this cyclization[4] reaction, we realized a 76% yield of 2,4,4-trimethyl-1-pentene, in 98% isomeric purity.

Discussion

The isomerization reaction proceeds quite rapidly at the temperatures and conditions required for the displacement reaction.[3] Consequently, we were originally concerned over the possibility that the two reactions would proceed concurrently. However, the isomerization reaction is powerfully catalyzed by the small excess of hydride normally used in the hydroboration stage.[4] In the displacement stage, the excess of the displacing olefin rapidly converts this catalyst into organoborane. With the catalyst absent, isomerization is no longer a serious side reaction.

The proposed mechanism for both the isomerization and displacement reactions involves a prior dissociation of the trialkylborane at the elevated temperature into a small equilibrium concentration of olefin and dialkylborane. Isomerization then involves a number of successive rapid readditions and eliminations until the boron atom accumulates in the most stable position in the molecule. In the presence of a large excess of extraneous olefin, the dialkylborane will tend to add to this unsaturate, rather than to the minute concentration of the eliminated product. Obviously an equilibrium would soon be established. However, by arranging conditions so that the displaced olefin is distilled out as formed, the reaction can be shifted to essential completion.

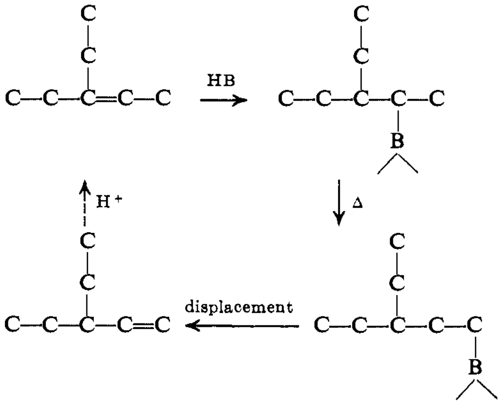
In the present study, we utilized the lower volatility of 1-decene to achieve the displacement of more volatile olefins. Obviously, it should be possible to utilize a large excess of some cheap olefin to accomplish the same end. Thus, Rutkowski has reported the synthesis of straight-chain α olefins by utilizing propylene, under pressure, to achieve the displacement.[7] Alternately, Sharma, *et al.*, utilized squalene to achieve the displacement of boron to achieve a synthesis of 1,3-cyclooctadiene.[8]

The present study suggests that olefins are liberated in the order of their stabilities. Thus 2-pentene is displaced more readily than 1-pentene. Similarly, 2-methyl-1-butene is displaced more readily than 3-methyl-1-butene. Similarly, it would appear that in the displacing reaction, 1-alkenes are more favorable than 2-methyl-1-alkenes.

Although the rate data are too approximate to attempt any quantitative correlation at this time, the results suggest that the stabler the olefin, as measured by its heat of combustion or heat of hydrogenation, the easier it is to displace and the less effective it is for displacement.

On this basis, the inertness of triethylboron in the displacement reaction[2] is a result of the high energy of the double bond in ethylene. Its heat of hydrogenation is considerably greater than that of other simple alkenes.[9] This suggests that a highly effective means of eliminating boron from a trialkylborane to form the olefin would be to treat the organoborane with ethylene under pressure at 160°. Unfortunately, we have not yet had an occasion to test this prediction.[10]

Treatment of olefins with strong acids or bases isomerizes the double bond from the terminal position to give the thermodynamically more stable secondary and tertiary olefins. It is evident that the present procedure afford a means of achieving the reverse isomerization (eq 2). Thus we may consider this process to involve the contrathermodynamic isomerization of olefins.



(2)

Experimental Section

Materials. The solvents, olefins, and the preparation of boron trifluoride diglymate have been described previously.[4] 1-Decene, from Humphrey-Wilkinson, Inc., was distilled from lithium aluminum hydride and stored over nitrogen.

Displacement Apparatus. The following apparatus was designed to permit following the displacement and recovery of highly volatile olefins with a minimum of loss. Hydroboration and isomerization were carried out in the usual manner[4] in a small flask. This was then attached to a Todd micro fractionating column, containing a 6-mm tube fitted with a wire spiral. The receiver consisted of a graduated cylinder which was equipped with a cooling jacket into which ice, or an ice–salt mixture, could be placed, and a stopcock, through which the product collected could be removed in increments for gas chromatographic examination. The receiver was so arranged that all vapors had to pass through the ice-cooled section before escaping out of the receiver into a trap maintained at −80°.

Displacement Procedure. Hydroboration was conducted by the internal method in the customary manner using diglyme as the solvent and sodium borohydride as the source of hydride.[4] Boron trifluoride diglymate was used to achieve hydroboration. The hydroboration was generally conducted at 25°, except in the case of highly volatile olefins, when the reaction was conducted with cooling by ice. The usual nitrogen atmosphere was used. In the normal procedure 100 mmoles of the olefin was treated with 30

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[6] H. C. Brown, K. J. Murray, H. Müller, and G. Zweifel, *J. Am. Chem. Soc.*, 88, 1443 (1966).

[7] A. J. Rutkowski, Preprints of Papers, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963.

[8] R. K. Sharma, B. A. Shoulders, and P. D. Gardner, *Chem. Ind.* (London), 2087 (1962).

[9] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, 57, 876 (1935).

[10] For commercial processes, where it would be important to recycle the boron values, it is obviously necessary to avoid the use of ethylene.

ml of a 1.00 *M* solution of sodium borohydride and 40 mmoles of boron trifluoride diglymate, providing 20% excess hydride. On completion of the reaction, checked by gas chromatographic examination for residual olefin, 150 mmoles of 1-decene (or other displacing olefin) was added and the flask (with adequate protection from atmospheric oxygen) was connected to the distillation assembly and brought to a rapid boil (the temperature in the flask was approximately 160°). The time for the appearance of the first drop of distillate was noted and considered as time zero. Individual fractions of 1.0, 2.0, 2.0 ml, etc., were collected in tared vials, weighed, and examined by gas chromatographic examination. The individual time for each fraction was noted and the times given in Table I represent the total elapsed time between the appearance of the first drop and the point at which the appearance of olefin became quite slow.

In the case of trisubstituted olefins hydroboration proceeds rapidly only to the dialkylborane stage. For these olefins, the procedure was varied to use 150 mequiv of hydride per 100 mmoles of olefin and 200 mmoles of 1-decene (or other olefin) for the displacement.

The recovery procedure was tested by introducing 100 mmoles of 1-pentene over a 3-hr period into refluxing diglyme. A 90% recovery was achieved. The yields reported in Tables I and II are actual yields and are not corrected for such normal operating losses.

Displacement Procedure with Isomerization. The hydroboration procedure was carried out precisely as described above. Following completion of the hydroboration, the reaction mixture was heated under gentle reflux for 1 hr to achieve isomerization. The reaction mixture was cooled to room temperature, the 1-decene was added, the flask was attached to the distillation assembly, and the displacement was carried out as described above.

Conversion of 3-Ethyl-2-pentene into 3-Ethyl-1-pentene. The following procedure is representative of those used to achieve the contrathermodynamic isomerization of olefins. 3-Ethyl-2-pentene, from the dehydration of triethylcarbinol,[4] was hydroborated in the usual manner, using 9.8 g, 100 mmoles, of the olefin, 30 mmoles of sodium borohydride, and 40 mmoles of boron trifluoride in diglyme. The reaction product was heated at gentle reflux for 1 hr. Then 21 g (150 mmoles) of 1-decene was injected by means of a syringe and the olefin formed was distilled through the Todd micro column. Over a period of 6 hr, five fractions were collected: 0.68, 1.62. 1.66, 1.63, and 1.52 g. Over another 9 hr, 0.86 g more was collected. The total yield was 7.97 g, 82% of theory. The gas chromatographic analysis established the composition to be 98% of 3-ethyl-1-pentene and 2% of 3-ethyl-2-pentene.

Organoboranes. V. The Thermal Cyclization of Dialkylboranes. A Convenient Synthesis of 2,4,4-Trimethyl-1,5-pentanediol and Related 1,5-Diols[1]

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Abstract: The isomerization of bis(2,4,4-trimethyl-3-pentyl)borane under the usual conditions results in the evolution of hydrogen and the formation of a boron heterocycle in addition to the usual primary alkyl derivative. Oxidation of the reaction mixture provides 2,4,4-trimethyl-1,5-pentanediol and 2,4,4-trimethyl-1-pentanol in close to a 1:1 mole ratio. The results reveal that under isomerization conditions dialkylboranes with five carbon atoms or more undergo an intramolecular substitution to produce the boron heterocycle and hydrogen. The reaction is especially facile in cases where primary hydrogen is available at the 5 position. Two general procedures were developed to achieve this cyclization: (1) the trialkylborane is first equilibrated with diborane to the dialkylborane stage, and then cyclized; (2) the olefin is reacted in a 1:1 ratio with thexylborane to produce the monoalkylthexylborane, which is then cyclized. The latter procedure provides more effective utilization of the starting olefin.

The hydroboration of internal olefins, followed by isomerization, generally provides the primary alkyl derivatives in yields of 90% or better.[4,5] Oxidation provides the primary alcohol[4,6] and displacement of the terminal olefin,[6] both in excellent yields.

However, in the case of 2,4,4-trimethyl-2-pentene, it was noted that the yields were consistently lower, in the neighborhood of 60%.[5,6] Investigation soon revealed that the dialkylborane was undergoing a facile cyclization, with evolution of hydrogen, to produce a boron heterocycle. Oxidation of this heterocyclic provided the glycol, 2,4,4-trimethyl-1,5-pentanediol.

This phase of our study was completed prior to 1960. At that time a number of publications appeared dealing with the thermal decomposition of trialkylboranes with the simultaneous formation of heterocyclic boron derivatives.[7,8] At that time we debated whether to continue our explorations in this area. However, for synthetic purposes there appeared to be definite advantages to our approach, based upon a deliberate synthesis of the dialkylborane. The latter offers the possibility of a 50% conversion of the initial olefin into the boron heterocycle, whereas the synthesis *via* the thermal decomposition of the trialkylborane possesses a natural limit of 33% conversion.[9] Accordingly, we decided to continue our examination of this approach. Indeed, we later discovered that the use of thexylborane[10] provides a means of converting suitable ole-

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